Vadose Zone Processes and Chemical Transport

Impact of Preferential Flow at Varying Irrigation Rates by Quantifying Mass Fluxes

T. J. Gish,* K.-J. S. Kung, D. C. Perry, J. Posner, G. Bubenzer, C. S. Helling, E. J. Kladivko, and T. S. Steenhuis

ABSTRACT

Solute concentration and soluble dye studies inferring that preferential flow accelerates field-scale contaminant transport are common but flux measurements quantifying its impact are essentially nonexistent. A tile-drain facility was used to determine the influence of matrix and preferential flow processes on the flux of mobile tracers subjected to different irrigation regimes (4.4 and 0.89 mm h⁻¹) in a silt loam soil. After tile outflow reached steady state either bromide (Br; 280 kg ha⁻¹) or pentafluorobenzoic acid (PFBA; 121 kg ha⁻¹) was applied through the irrigation system inside a shed (3.5 \times 24 m). Bromide fluxes were monitored at an irrigation rate of 4.4 mm h⁻¹ while PFBA fluxes were monitored at an irrigation rate of 0.89 mm h⁻¹. At 4.4 mm h⁻¹ nearly one-third of the surface-applied Br was recovered in the tile line after only 124 mm of irrigation and was poorly fit by the one-dimensional convective-dispersive equation (CDE). On the other hand, the one-dimensional CDE fit the main PFBA breakthrough pattern almost perfectly, suggesting the PFBA transport was dominated by matrix flow. Furthermore, after 225 mm of water had been applied, less than 2% of the applied PFBA had been leached through the soil compared with more than 59% of the applied Br. This study demonstrates that the methodology of applying a narrow strip of chemical to a tile drain facility is appropriate for quantifying chemical fluxes at the small-field scale and also suggests that there may be a critical input flux whereby preferential flow is initiated.

During the past three decades, considerable research has been conducted to alleviate the undesirable trade-off between production of food and fiber and the deterioration in ground water quality (Posner et al., 1995). At the same time, development of chemical transport models has proceeded at a much faster rate than model validation (Wagenet and Rao, 1990). Under well-controlled conditions, some observed breakthrough patterns can be simulated. However, our inability to accurately monitor field-scale mass fluxes is the most significant factor limiting the development of accurate chemi-

T.J. Gish, Hydrology and Remote Sensing Laboratory, and C.S. Helling, Alternate Crops and Systems Laboratory, USDA-ARS, BARC-West, 10300 Baltimore Boulevard, Beltsville, MD 20705-2350. K.-J.S. Kung, Department of Soil Science, J. Posner, Agronomy Department, and G. Bubenzer, Department of Biological System Engineering, University of Wisconsin, Madison, WI 53706-1299. D.C. Perry, Civil Engineering Department, Santa Clara University, 500 Camino Real, Santa Clara, CA 95053. E.J. Kladivko, Department of Agronomy, Purdue University, West Lafayette, IN 47906. T.S. Steenhuis, Department of Agricultural and Biological Engineering, Cornell University, Ithaca, NY 14853. Trade names are included for the benefit of the reader and imply no endorsement or preferential treatment of the product listed by the U.S. Department of Agriculture. Received 1 July 2002. *Corresponding author (tgish@hydrolab.arsusda.gov).

Published in J. Environ. Qual. 33:1033–1040 (2004). © ASA, CSSA, SSSA 677 S. Segoe Rd., Madison, WI 53711 USA cal transport models. Furthermore, three additional obstacles that limit our understanding of contaminant transport in unsaturated soils are: (i) insufficient data to represent a given flow or biological process, (ii) lack of methods for measuring certain flow-related parameters (especially true for multiphase flows and kinetic processes), and (iii) insufficient knowledge of the processes governing chemical transport at the scale of interest (National Research Council, 1988). Without the ability to monitor a total subsurface flux in the field, it is not surprising that scientific interpretation of randomly located soil core and well-log data has made model predictions nearly impossible and environmental policy difficult (Cohen et al., 1986; Gustafson, 1989).

To quantify a chemical flux, leaching from matrix and preferential flow processes must be simultaneously monitored. The mechanisms governing transport through matrix pores have been thoroughly documented (Biggar and Nielsen, 1967; Dagan and Bresler, 1979; Jury et al., 1991). To fully comprehend preferential flow and develop theory to describe its behavior and impact, it is crucial to first quantitatively determine when preferential flow will become hydraulically active under field conditions. Sampling tile drains is an attractive method for directly measuring the total mass flux of chemicals associated with leaching under field-scale conditions (Richards and Steenhuis, 1988; Kanwar et al., 1988; Kladivko et al., 1991; Zehe and Fluhler, 2001). Nevertheless, unless tiles are closely spaced, some of the uniformly applied chemicals that reach the shallow ground water would inevitably be transported either vertically into regional ground water or laterally (parallel to the tile) away from the field (Flury, 1996; Wells et al., 1998). Furthermore, it takes additional time for chemicals leached to the shallow water table to be transported horizontally through the saturated zone to the tile line. This additional time for horizontal transport masks the true chemical breakthrough time within unsaturated soil, which is a critical parameter at the field scale (Skaggs et al., 1998). Radcliffe et al. (1996) used a twolayer approach to derive parameters such as field-scale dispersivity of an unsaturated profile. However, a relatively accurate two-dimensional model for flow through the saturated zone was required.

Kung et al. (2000a) developed a field-scale solute flux approach that minimizes the drawbacks of using the tile-drained system to determine a solute leachate flux through an unsaturated profile. In this method, tracers

Abbreviations: CDE, convective-dispersive equation; PFBA, penta-fluorobenzoic acid.

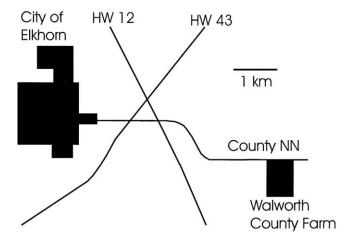
or chemicals of interest are applied to a narrow strip parallel to the tile lines (typically 3 × 24 m) even though the entire field is irrigated. Using this technique, the authors sequentially applied four conservative tracers and found that not all preferential flow paths were simultaneously active during irrigation. This work not only confirmed that antecedent moisture plays a critical role in dictating which preferential flow pathways become hydraulically active (Beven and Germann, 1982; Edwards et al., 1988; Kumar et al., 1997; Keppeler and Brown, 1998), but also provided a valuable method for monitoring an undisturbed solute leachate flux in the field.

Everts and Kanwar (1990) and Lennartz et al. (1999) collected chemical breakthrough patterns from a tile drain to estimate the impact of field-scale preferential flow paths. Kumar et al. (1997) used sudden change in the slope of a tile drain hydrograph to partition preferential flow from matrix flow. These experiments were conducted under transient conditions where soil water content changed continuously. As shown by the breakthrough patterns of sequentially applied tracers in Kung et al. (2000a), the matric potential gradient could cause significant lateral movement of water-borne tracers from preferential flow paths to matrix pores under transient unsaturated conditions. In other words, contaminants being transported downward through the upper part of a certain preferential flow path could be sucked into matrix pores at the lower part of a soil profile under transient conditions. This allows some preferential flow pathways to initially behave like truncated channels (i.e., dead-end pores). The drier a soil profile, the more likely preferential flow paths would initially behave like deadend pores. Therefore, chemical breakthrough patterns or hydrographs collected under transient conditions cannot be generalized to characterize the pore spectrum of preferential flow paths. In the literature, no research has been conducted that attempts to quantify the impact preferential flow paths have on field-scale solute mass flux as a result of near-steady-state conditions.

The objective of the study was to determine the relative importance of field-scale matrix and preferential flow processes on transport of mobile chemicals under steady-state infiltration rates. The partial area tracer approach by Kung et al. (2000a, 2000b) was used on a tile-drain monitoring facility so that total solute mass flux, including preferential and matrix flow processes, could be accurately monitored. Solute fluxes observed under two near-steady-state infiltration regimes were fitted and evaluated using the classical convection–dispersive equation.

MATERIALS AND METHODS

Field experiments were conducted in early summer of 1999 at the Walworth County Farm in Elkhorn, Wisconsin. The research site is located within the Southern Wisconsin and Northern Illinois Drift Plain (42°42′ N, 88°32′ W; Fig. 1). The area has gone through an evolution of primarily continuous small grains, to dairy, to cash grain corn (*Zea mays* L.)–soybean [*Glycine max* (L.) Merr.] systems. Generally, these soils are characterized by a silt loam surface horizon (0–35 cm,



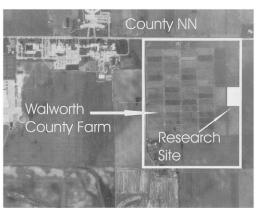


Fig. 1. Experimental site location.

3% organic matter), followed by a clay-loam or sandy clay-loam B horizon (35–65 cm), and underlain by glacial well-mixed gravelly till. Average depth to compacted glacial till is between 80 and 130 cm, and the soils are classified as Pella silt loam (fine-silty, mixed, mesic Typic Endoaquolls). These prairie-derived silt loam soils cover the southeastern part of Wisconsin into northern Illinois and represent some of the most productive agricultural lands in this region.

The research facility for this study consisted of a 160-by 72-m tile-drained field plot (Fig. 2). The field has a slope between 1 and 3% and has been under a no-till corn-soybeanwheat (Triticum aestivum L.) rotation for 12 yr. In 1970, tile drains with uniform 18-m spacing were buried at around 0.9 to 1.1 m deep. Independent studies conducted in Iowa (Kumar et al., 1997) and at the Willsboro Farm of Cornell University (Shalit et al., 1995) showed that, after a soil profile was healed, contaminant transport through preferential flow paths was not caused by the installation of the tiles. Since the tile drains had been installed about 30 yr earlier, it is very unlikely that tile installation would affect the transit times of chemicals in this study. A manhole down-gradient of the field was installed in 1997. Flow rate of the tile drain was continuously recorded by using a submerged pressure transducer (KPSI Pressure Systems, Hampton, VA) to measure water height in a flume with a 15° V-shaped, sharp-edged notch.

Soybeans had just emerged when the tracer experiment was initiated. A steady 4 mm h⁻¹ irrigation was applied to two 16- by 30-m areas near the three central tile lines through two rows of solid-state sprinklers. Each row of sprinklers had three nozzles (Fig. 2). This rate was chosen because ponding occurred in a preliminary study where 4 mm h⁻¹ was applied.

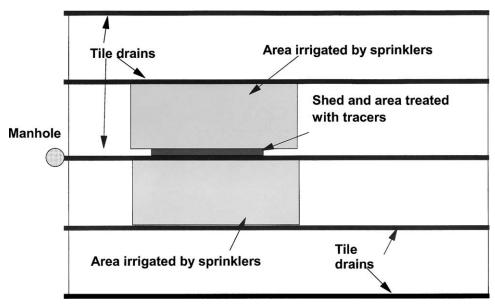


Fig. 2. Schematic of the tile-drained facility.

A 3.5- by 24-m shed was located between the two rows of solid-state sprinklers. The aluminum-framed shed was 1.5 m high and the walls and roof were made of corrugated polycarbonate sheet that had about 90% light transparency. The long side of the shed was parallel to the tile line offset 0.3 m to further minimize any potential impact of tile-drain installation 30 yr prior. The shed was 15 m from the manhole. Water collected from the roof of the shed during natural precipitation events was diverted away from the field by gutters. Eight carefully calibrated nozzles were used inside the shed. These nozzles were oscillating inside the shed, similar to the design of Ghodrati et al. (1990) and Radcliffe et al. (1996). However, the nozzles were 2.4 m apart and mounted on a trolley and oscillating along the long side of the shed. This design offered around 90 to 95% Christiansen uniformity (Christiansen, 1942) inside the shed under all climatic conditions, while that of the outside irrigation varied from around 20 to 85% depending primarily on the wind conditions. Metal flashing was installed around the sides of the shed to prevent outside runoff from entering the shed during heavy precipitation events.

Using the Kung partial area flux approach, the study area near the tile drain is subjected to one set of conditions (unique tracers, irrigation rate, etc.), while the soil surrounding the study area is irrigated at a rate sufficient to keep the water table from falling below the tile lines while avoiding saturating the soil surface. As a result, during the first phase of the study, the irrigation rate inside the shed was 4.4 mm h⁻¹ while on the outside the irrigation rate was maintained at 4 mm h⁻¹. The irrigation within the shed was very uniform and its intensity was less than the saturated conductivity of the soil. The tile flow was continuously monitored after irrigation started. Two days after the tile outflow became steady state, a pulse of conservative tracer, potassium bromide solution (2350 g Br or 280 kg Br ha⁻¹), was applied from the nozzles inside the shed. No Br was applied outside the shed. During tracer application, irrigation rates inside and outside the shed were maintained. Water samples from the tile drain were manually collected once every 2 min during the first 2 h after tracer application. Following the first 2 h of tracer application, water samples were collected using an automated sampler (Isco, Lincoln, NE). After the first 2 h, tile drain samples were collected every 6 min during the next 10 h. During the subsequent 12 h the sampling interval was 15 min, which was then increased to 1 h for the next 3 d and finally every 2 h for the last 10 d. Flow rates of the tile drain were continuously monitored by pressure transducer and manually measured at least twice a day.

Irrigation was stopped 22 d after Br application and the entire field was allowed to drain for a week. To estimate bromide mass remaining in the soil profile, five 75-cm cores were randomly removed from the treated area. Each core was 10.2 cm in diameter and segmented into 7.5-cm depth increments. By the time the first irrigation study was concluded, the soybean plants had reached a height of about 0.25 m. Because a thin layer of algae started to grow on the soil surface inside the shed, we decided to move the entire irrigation system laterally, 0.3 m off center to the other side of the tile drain (0.6 m away from the Br study). A mower was first used to cut the soybeans to about a 0.10-m height on a 5- by 40-m strip along the opposite side of the tile line shortly before the shed was moved to the new location.

During the second phase of the study the irrigation intensity inside the shed was reduced to 0.89 mm h⁻¹, while that of the outside was maintained at 4 mm h^{-1} . To decrease the irrigation rate inside the shed it was necessary to either decrease water pressure applied to the nozzles or use different nozzles. We searched and could not find nozzles that could uniformly administer an irrigation rate as low as 0.89 mm h⁻¹ throughout the entire shed. It was unacceptable to decrease water pressure because the uniformity decreases sharply as the pressure decreases. Therefore, water was again applied at a 4.4 mm h⁻¹ rate but in an intermittent fashion about one quarter of the time, yielding an irrigation rate of 0.89 mm h^{-1} . Note that the irrigation rate outside the shed was constant during the two tracer experiments and the outside irrigated area was much larger than within the shed. As a result, the impact of changing the irrigation rate within the shed on the overall ground water table height and flow pattern within the saturated zone was minimized. This ensured that if differences occurred between the two phases of this experiment, it would be a result of what happened within the shed (i.e., different irrigation regimes instead of the chemical transport within the saturated zone). The large areas (84 m²) being monitored for a chemical flux and small distance between the regions under investigation (0.6 m apart) minimize any potential impact of soil heterogeneity dramatically influencing small field-scale transport. In addition, because of the low irrigation rates used in both phases of this study, water did not pond inside the shed.

Two days after the tile drain reached steady state at the lower irrigation rate, a pulse of a mobile conservative tracer, pentafluorobenzoic acid (493.5 g of PFBA), was applied from the nozzles inside the shed. No PFBA tracer was applied outside the shed area. According to Jaynes (1994) and Kung et al. (2000a), PFBA is as conservative as Br and has an almost identical breakthrough pattern as that of Br. Water samples were collected with identical frequency after tracer application. Theoretically, the sampling period of the second experiment should be longer than the first experiment. However, the experiment was ended at only 14 d after tracer application because we noticed that the overall water table height in the experimental area started to drop as regional evapotranspiration rates increased. The increase in evapotranspiration rates outside the shed could influence the transport within the saturated zone, thus affecting chemical transport near the tile drains. Soil samples with a 7.5-cm increment and 10.2-cm diameter were again collected from four 75-cm soil cores at random locations inside the shed to estimate PFBA mass left in soil profile.

RESULTS AND DISCUSSION

Figure 3 shows tile fluxes as a function of time for the first phase of the study (i.e., Br transport). With an irrigation rate of 4.4 mm h⁻¹ inside the shed and 4 mm h^{−1} outside the shed the tile drain reached a steady-state flow rate of 200 mL s⁻¹. Although irrigation intensities inside and outside the shed were maintained constant. tile flow did have minimal diurnal fluctuations due to evapotranspiration outside the shed. Nonetheless, steadystate flow conditions were maintained during the first 30 h after Br application. However, between 35 and 60 h after tracer application, there were heavy but shortduration thunderstorms, which caused sharp increases in tile drain flow. After the second precipitation event, the irrigation outside the shed was shut off because water started to pond on the soil surface outside the irrigation shed and surface runoff began. Nevertheless, because metal flashing was installed around the shed, no runoff entered the shed.

Due to natural rainfall events and unexpected power outage, the tile flow fluctuated on several occasions. In spite of the temporal fluctuations in tile drainage, the Br breakthrough curve had a very distinct pattern common to flow systems dominated by preferential flow (Fig. 3). Bromide mass flux at 0.95 m below the soil surface quickly increased two orders of magnitude within only 6 h of application, then was essentially constant from 6 to 60 h, after which the flux started to tail off gradually. No significant Br mass was recovered in the tile drains after 10.3 d of application. The initial arrival of Br was detected in the tile drain after only 16 min from application. An approximate pore volume for this soil would be about 350 mm of irrigation water. However, after only 80 mm infiltrated, more than 19% of the surface-applied Br had leached through the soil to the tile drain. By the time 124 mm of irrigation had been applied, more than 33% of the surface-applied Br had leached through the root zone to the tile drain. Under lab measurements, the saturated hydraulic con-

ductivity of homogenized soil samples taken from the soil profile ranged from 3 to 20 mm h⁻¹. Using the classical convection-dispersion transport theory and laboratory hydraulic conductivity values it should have taken at least 30 h before Br would reach the tile drain. Short Br transit times monitored from the tile drain and the rapid rise of the breakthrough curves indicate that Br was being primarily transported through preferential flow pathways. In another tracer experiment, Kung et al. (2000a) applied fluorobenzoic acid 6 h after an irrigation with 3 mm h^{-1} intensity in the Clermont silt loam (finesilty, mixed, superactive, mesic Typic Glossaqualfs) of the South East Purdue Agricultural Center of Purdue University in Butlerville, Indiana, where the same tiledrain protocol (except tile-drain flow was transient and not approaching steady state) was used to monitor chemical transport. The Purdue results showed that the breakthrough of fluorobenzoic acid tracer in the tile occurred 18 min after tracer application.

In the second phase of this study, an irrigation rate of 0.89 mm h⁻¹ inside the shed and 4 mm h⁻¹ outside the shed was attempted. The resulting tile drain flow reached steady state at 140 mL s⁻¹. The observed steady-state flow rate from the tile drain again had slight diurnal fluctuation because of evapotranspiration (Fig. 4). Four major natural precipitation events occurred from 90 to 300 h after tracer application and each event caused a sharp increase of the tile flow hydrograph beyond our control. Nevertheless, the infiltration within the shed was maintained at steady state. Because the shutting off and turning on of the outside irrigation was better controlled during the second tracer experiment, the tile flow never dipped below a steady-state rate of 140 mL s⁻¹.

Figure 4 shows that very low amounts of PFBA were detected sporadically in the tile drain during the first 90 h after application. The background PFBA concentration was zero and the concentrations from samples collected during this period were well above the detection limit of 10 µg L⁻¹. Early breakthrough suggested that preferential flow paths participated in the transport of PFBA even under a low steady-state infiltration rate of 0.89 mm h⁻¹. However, we believed that this early arrival during the first 90 h was caused by the oscillating sprinkler irrigation system. If we had applied irrigation under a true steady 0.89 mm h⁻¹ rate, the early PFBA breakthrough probably would not have happened. Nevertheless, even with our approach less than 0.004% of the applied PFBA mass had leached through the soil to the tile drains after 90 h. Therefore, although there was early breakthrough, the impact of preferential flow caused by the intermittent water application on the transport of PFBA was insignificant.

Ninety hours after PFBA application the main PFBA breakthrough started to emerge (Fig. 4). This main breakthrough curve peaked at around 240 h after tracer application. This slow breakthrough curve was not observed in the Br transport that was dominated by preferential flow. The shape of the PFBA breakthrough pattern suggested that matrix flow through the smaller matrix pores of the soil was the dominant transport

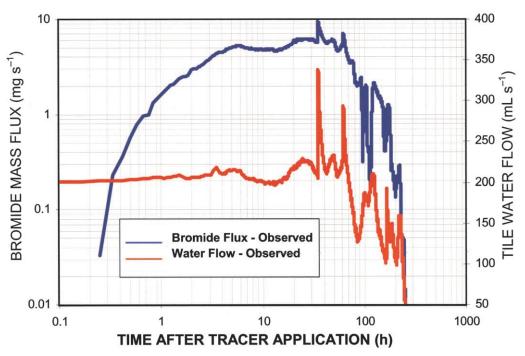


Fig. 3. Water flux and Br breakthrough curves. The red line represents water flux while the blue line denotes bromide mass flux as a function of time after application. Bromide mobile tracer was subjected to a 4.4 mm h⁻¹ irrigation rate.

mechanism. To confirm this assessment, the one-dimensional steady-state analytical solution of the CDE by Van Genuchten and Alves (1982) and Jury et al. (1991) was used to fit the PFBA mass breakthrough pattern. The analytical solution has only three parameters: water velocity V, apparent dispersion coefficient D, and soil profile depth L. Water velocity was calculated from the

irrigation rate (0.89 mm h⁻¹) divided by the effective soil water content θ , which was $0.32 \, \mathrm{cm^3 \, cm^{-3}}$ (measured from four 30-cm soil core samples taken shortly after the experiment). We chose 0.95 m for the average depth to tile drain. The dispersion coefficient D was not measured during the experiment and was the only adjustable parameter in achieving the best fit. The fitted analytical

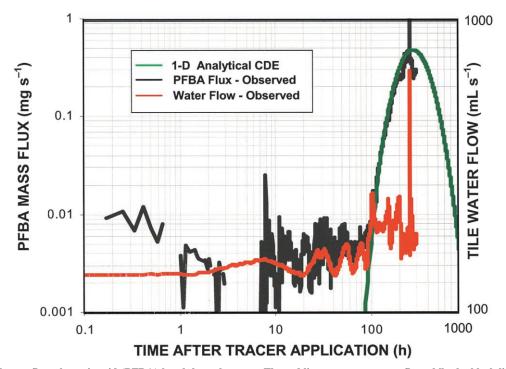


Fig. 4. Water and pentafluorobenzoic acid (PFBA) breakthrough curves. The red line represents water flux while the black line denotes PFBA mass flux as a function of time after application. The PFBA mobile tracer was subjected to a 0.89 mm h⁻¹ irrigation rate. The green line represents the best fit line using the one-dimensional convective-dispersive equation (CDE).

result is shown as a smooth green line in Fig. 4. A dispersion coefficient D of 5 \times 10 ⁻⁸ m² s⁻¹ gave the best fit. This D value was close to many laboratory measurements based on transport of conservative tracers in homogenized silt loam soils (Elrick, 1980; Gish and Jury, 1983; Schwartz et al., 2000). The nearly perfect fit $(r^2 = 0.997)$ between the measured breakthrough pattern and the analytical solution, from 0.003 to more than 36% of the recovered tracer (Fig. 5), suggests that under a steady-state rate of 0.89 mm h⁻¹, almost all of the tracer was transported through a matrix flow process (i.e., no significant preferential flow). The total PFBA mass recovered from the tile during the entire sampling period, 320 h, was 36.2% of the total mass applied. Note that when the irrigation was stopped, the breakthrough of PFBA had just passed its peak value and was gradually tailing off. In other words, if the tail of the PFBA breakthrough was similar to that of the one-dimensional CDE analytical solution, the total PFBA mass recovered would have reached 99%.

Based on five soil cores, the calculated Br mass recovered from the top 75 cm of soil within the shed was 78.7 g (3.35% mass applied), while that of the PFBA was 4.37 g (0.89% mass applied). There was considerable variation among the solute masses recovered from these soil cores. The range in Br recoveries per core was 13.8 and 3.47 g, respectively, while those of PFBA were 0.9 g and 0.011 g, respectively. This again demonstrates the uncertainty that is typically encountered when using soil core data alone to quantify contaminant transport.

To directly compare the differential solute transport through different pathways caused by difference in irrigation rates, the tracer mass recovery was normalized by mass applied. Figure 5 shows the amount of Br and PFBA leached through the soil to tile drains (relative to that applied) as a function of cumulative water applied. After 225 mm of irrigation water had been applied, <2% of the PFBA had been leached through the soil at the low irrigation rate of 0.89 mm h⁻¹. In comparison, >59% of the Br had leached through the soil after 225 mm of irrigation water (applied at 4.4 mm h⁻¹). The dramatic difference in transport times for these mobile tracers at two different irrigation rates suggests a different mechanism is responsible for their transport.

It has been traditionally perceived that the total amount of net infiltration would dictate the vertical chemical transport and could be used to replace real time in simulations (Wierenga, 1977; Jury and Roth, 1990). As a result, many deterministic and stochastic models have used net infiltration, in lieu of real time, as an input parameter to drive contaminant transport. The difference between Br and PFBA in Fig. 5 indicates that, when preferential flow pathways become hydraulically active, the total amount of net infiltration alone no longer dictates the vertical chemical transport.

The one-dimensional analytical solution was used to calculate what the bromide breakthrough pattern would have been if it followed the same flow mechanisms as PFBA. Again, the only parameter not measured was the apparent diffusion coefficient, D, which would increase as flow velocity V increases (Gish and Jury, 1983).

Two apparent diffusion coefficients were chosen. For Br the first D was estimated as 10^{-7} , which was twice that used to achieve the best fit for the PFBA breakthrough (Fig. 6). As water flux increases from 0.89 to 4.4 m h^{-1} , it is reasonable to expect that D would increase by at least a factor of two. However, the calculated Br breakthrough pattern based on this value is much slower than the observed values based solely on flux observations. As a result, we calculated the one-dimensional breakthrough pattern again by increasing D by a factor of 10 to 10^{-6} m² s⁻¹. Nevertheless, the calculated Br breakthrough pattern based on this value (as shown in Fig. 6) is still clearly slower than the measured pattern. The dramatic increase of Br relative to the PFBA under identical water inputs reinforces the importance of comprehending and quantifying transport mechanisms to predict contaminant transport in unsaturated soils. It has been conventionally practiced to calibrate a model under a flow rate and then apply the model to predict contaminant transport under other flow rates. Our results suggest that, when different flow mechanisms become active, previously derived parameters may likely become invalid.

This experiment not only confirms the appropriateness of using the partial area tile-drained protocol for quantifying solute fluxes but also indicates that there may be a critical input rate for each soil whereby preferential fluid dynamics and not matrix flow dominates chemical transport. Additional field studies using a range of steady-state infiltration rates are justified so that the water input rate where preferential flow dominates transport can be quantified. Soils in different hydrogeologic settings also need to be evaluated using this protocol since pore geometry, structure, and stability may be dissimilar between different hydrologic units.

CONCLUSIONS

A tile-drain monitoring facility was used to examine chemical leaching through preferential and matrix pathways under two steady-state infiltration conditions. Results from the PFBA experiment showed that the main breakthrough did not occur until 90 h after tracer application and peaked at around 240 h after tracer application. The measured PFBA breakthrough pattern coincided with an analytical solution based on one-dimensional CDE. The nearly perfect fit suggested that, under a steady-state infiltration rate of 0.89 mm h⁻¹, the mobile tracer was completely transported through the small matrix pores.

Results from the Br breakthrough pattern showed that chemical arrival occurred within 16 min after tracer application and that the peak of breakthrough curve occurred within the first 10 h. With less than 80 mm of irrigation applied, more than 19% of the surface-applied Br had leached through the soil root zone. This suggested that preferential flow paths were initiated at a steady-state infiltration rate of 4.4 mm h⁻¹ and played a significant role in contaminant transport in a field soil profile.

It has been traditionally perceived that the total

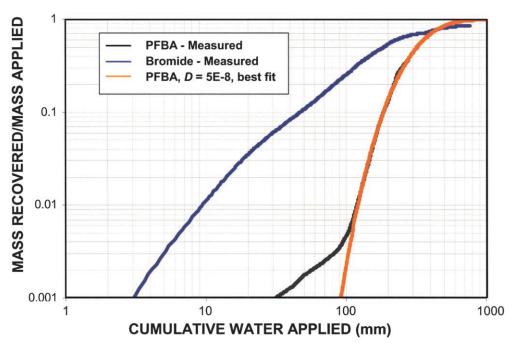


Fig. 5. Comparison of Br and pentafluorobenzoic acid (PFBA) breakthrough curves as a function of water applied. The blue line represents the Br breakthrough pattern at an irrigation rate of 4.4 mm h⁻¹ while the black line denotes the PFBA breakthrough pattern at an irrigation rate of 0.89 mm h⁻¹. The orange line represents the best fit line using the one-dimensional convective-dispersive equation (CDE) of the PFBA data. Solute recoveries and transport fitting are a function of cumulative water applied since tracer application.

amount of net infiltration would dictate the vertical chemical transport. Many models have used net infiltration to replace real time in simulations of vertical chemical leaching. Our results demonstrated that, when preferential flow pathways become hydraulically active, it is

critical to partition total applied water into two different types of flow pathways. Parameters derived from fitting breakthrough patterns at lower infiltration rates cannot be used to predict the fast breakthrough pattern caused by preferential flow.

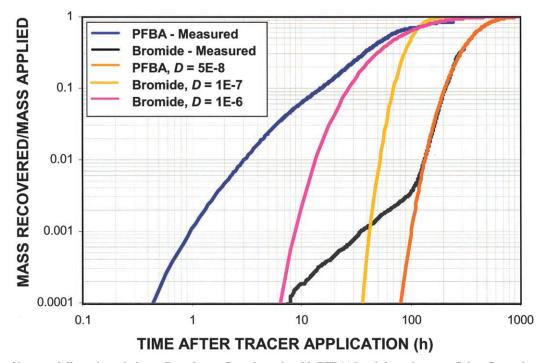


Fig. 6. Effect of increased dispersion relative to Br and pentafluorobenzoic acid (PFBA) breakthrough curves. Solute fluxes shown as a function of time after application. Blue and black lines represent Br and PFBA breakthrough patterns at irrigation rates of 4.4 and 0.89 mm h⁻¹, respectively. The orange line represents the best fit line using the one-dimensional convective-dispersive equation (CDE) on the lower irrigation rate (PFBA) while at the higher irrigation rate (Br) transport simulations were conducted by increasing the dispersion coefficient by 2 (gold line) and 10 times (pink line).

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